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(54) **Process for dispersing ignition resistant additives into carbonate polymers.**

(57) A process for dispersing one or more powdered ignition resistant or flame retardant additives into carbonate polymers which comprises the steps of preparing a base concentrate having from 5 to 50 weight per cent of said additives by blending said additives with a carbonate polymer having a melt flow rate of from 3 to 20, pelletizing said base concentrate having said ignition resistant additive dispersed therein, dry blending said concentrate pellets with carbonate polymer pellets having a melt flow rate of from 1 to 80 whereby said polymer/concentrate blend has an amount of said additive dispersed therein effective to render said blend ignition resistant, and pelletizing or molding said carbonate polymer/concentrate blend. The use of this method gives ignition resistant carbonate polymers with improved impact properties as measured by Izod impact tests.

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PROCESS FOR DISPERSING IGNITION RESISTANT ADDITIVES INTO CARBONATE POLYMERS

This invention relates to a composition and a process for the production of ignition resistant or flame retardant polycarbonates and/or carbonate polymers wherein the ignition resistant additives are first compounded into a polycarbonate carrier resin then blended with a low molecular weight or moldable polycarbonate.

5 It is known from U.S. Patent No. 4,626,563 that aromatic sulfimide metal salts, monomeric or polymeric halogenated aromatic compounds, metal salts of inorganic acids having a pKa of from 1 to 5, and fibril-forming polytetrafluoroethylene are useful to render carbonate polymers ignition resistant or flame retardant. Other flame retardant additives are known from and listed in U.S. Patent No. 4,650,823. These patents are incorporated by reference herein.

10 The present invention is broadly directed to a process for dispersing one or more powdered ignition resistant or flame retardant additives into carbonate polymers wherein the impact properties of the ignition resistant carbonate polymers is improved.

More specifically, the invention is directed to a process for dispersing one or more powdered ignition resistant or flame retardant additives into carbonate polymers which comprises the steps of preparing a
15 base concentrate having from 5 to 50 weight per cent of said additives by blending said additives with a carbonate polymer having a melt flow rate (MFR) of from 3 to 80 and preferably a MFR in the range of from 3 to 20, pelletizing said base concentrate having said ignition resistant additive dispersed therein, dry blending said concentrate pellets with carbonate polymer pellets having a melt flow rate of from 1 to 80 whereby said polymer/concentrate blend has an amount of said additive dispersed therein effective to
20 render said blend ignition resistant, and pelletizing or molding said carbonate polymer/concentrate blend.

The process of this invention has the following steps:

A) preparing a base concentrate by blending a carbonate polymer having a melt flow rate in the range of from 3 to 80 with an additive composition comprising

- i) 2.0 to 10 percent by weight of a metal salt of an aromatic sulfur containing compound,
- 25 ii) 10 to 80 percent by weight of a monomeric, oligomeric or polymeric halogenated aromatic compound,
- iii) 2.0 to 10.0 percent by weight of a compound selected from a metal salt of an inorganic compound and a free aromatic sulfimide, and
- iv) 6 to 40 percent by weight of a fibril-forming polytetrafluoroethylene;

30 B) blending said base concentrate pellets with carbonate polymer pellets having a melt flow rate of from 1 to 80 and substantially lower than that of said first carbonate polymer whereby the additive composition in said polymer/concentrate blend is present in an amount effective to render said blend ignition resistant; and

C) pelletizing or molding said carbonate polymer/concentrate blend.

35 The advantages of the invention over the known techniques are that significant improvement is seen in the toughness of the final product as measured by improved Izod impact tests when the polymer concentrate is first made and diluted down with additional polymer. In addition, the generation of dust particles which is commonly found in additive compounding is eliminated.

The carbonate polymers employed in the present invention are advantageously aromatic carbonate
40 polymers such as the trityl diol carbonates described in U.S. Patent Nos. 3,036,036; 3,036,037; 3,036,038 and 3,036,039; polycarbonates of bis(ar-hydroxyphenyl) alkylidenes (often called bisphenol-A type diols) including their aromatically and aliphatically substituted derivatives such as disclosed in U.S. Patent Nos. 2,999,835; 3,038,365 and 3,334,154; and carbonate polymers derived from other aromatic diols such as described in U.S. Patent No. 3,169,121.

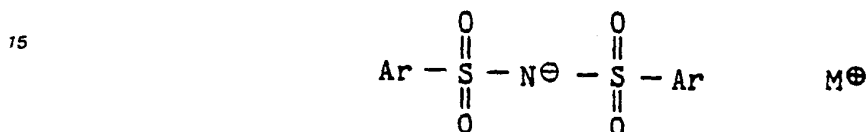
45 It is understood, of course, that the polycarbonate may be derived from (1) two or more different dihydric phenols or (2) a dihydric phenol and a glycol or a hydroxy- or acid-terminated polyester or a dibasic acid in the event a carbonate copolymer or heteropolymer rather than a homopolymer is desired. Also suitable for the practice of this invention are blends of any one of the above carbonate polymers. Also included in the term carbonate polymer are the ester/carbonate copolymers of the types described in U.S.
50 Patent Nos. 3,169,121; 4,105,633; 4,156,069; 4,225,556; 4,260,731; 4,287,787; 4,330,662; 4,355,150 4,360,656; 4,374,973; and 4,388,455. Of the aforementioned carbonate polymers, the polycarbonates of bisphenol-A and derivatives, including copolycarbonates of bisphenol-A, are preferred. Methods for preparing carbonate polymers for use in the practice of this invention are well known. For example, several suitable methods are disclosed in the aforementioned patents.

The monomeric, oligomeric or polymeric halogenated aromatic compound used in this invention can be

virtually any halogenated organic compound commonly used as a fire retardant additive. The preferred compounds are the halo-substituted aromatic compounds (halo is fluoro, chloro, or bromo). Suitable compounds include, for example, decabromo diphenyl oxide, tris(tribromophenoxy) triazine, decabromodiphenyl carbonate, an oligomer or polymer of tetrabromobisphenol A, and a copolymer of bisphenol A/tetrabromobisphenol A. Combinations of the above identified compounds can be employed. Examples of other suitable monomeric and polymeric halogenated compounds are disclosed in U.S. Patent No. 4,263,201.

The metal salts of sulfur compounds used herein include metal salts of aromatic sulfonates, sulfates, sulfonamides, and sulfimides. Suitable metals are the metals of Groups I and IIA of the Periodic Chart as well as copper, aluminum, and antimony. The preferred metal is an alkali metal such as sodium or potassium.

The preferred group of aromatic sulfur compounds are sulfimides having the formula



wherein Ar is an aromatic group and M is a metal cation.

Examples of the sulfimide salts are the alkali metal salts of saccharin, N-(p-tolylsulfonyl)-p-toluene sulfimide, N-(N-benzylaminocarbonyl)sulfanilimide, N-(phenylcarboxyl)-sulfanilimide, N-(2-pyrimidinyl)-sulfanilimide, and N-(2-thiazolyl)sulfanilimide. These salts and similar ones are disclosed in U.S. Patent No. 4,254,015.

The free aromatic sulfimides useful in this invention are those having a pKa in the range of from 1 to 3. Examples of such free aromatic sulfimides are saccharin, N-(p-tolylsulfonyl)-p-toluene sulfimide, N-(N-benzylaminocarbonyl)sulfanilimide, N-(phenylcarboxyl)-sulfanilimide, N-(2-pyrimidinyl)-sulfanilimide, and N-(2-thiazolyl)sulfanilimide. They are further illustrated by the formula



wherein R is carbonyl, arylcarbonyl, arylaminocarbonyl, aralkylaminocarbonyl, or arylsulfonyl. Specific examples of these groups are benzoyl, benzylaminocarbonyl and tolylsulfonyl groups.

In general, the additive package has a fixed weight ratio of components so that after the polymer concentrate is made it can be readily shipped without dust formation to desired locations where it can be diluted down or let down with more polymer to the final ignition resistant product. The preferred ratio of the components, metal salt of an aromatic sulfur containing compound : monomeric, oligomeric or polymeric halogenated aromatic compound : metal salt of an inorganic compound : fibril-forming polytetrafluoroethylene is 1:10:1:3. For example, a 15 percent additive/polymer concentrate is blended with more polymer at a 10:1 ratio to give a useful ignition resistant blend.

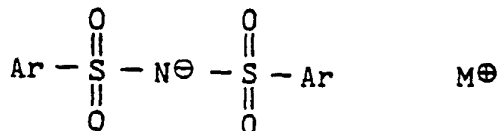
In addition to the aforementioned fire retardant additives, other additives can be included in the carbonate polymer composition of the present invention such as fillers (i.e. glass fibers), pigments, dyes, antioxidants, stabilizers, ultraviolet light absorbers, mold release agents, impact modifiers and other additives commonly employed in carbonate polymer compositions.

The following examples and controls are presented to further illustrate the invention.

Example 1

A fifteen percent ignition resistant (IR) polycarbonate concentrate was prepared by adding 1 gram (1 percent) potassium paratolylsulfimide (KPTSM), 1 gram (1 percent) potassium bisulfate (KHSO₄), 3 grams (3 percent) fibril-forming polytetrafluoroethylene (Teflon 6C) and 10 grams (10 percent) tetrabromobisphenol-A

oligomer (TBBPA), all in one masterbatch, to 85 gms (85 percent) heat stabilized polycarbonate resin having a 22 gms/10 min MFR (melt flow rate). The KPTSM is represented by the formula:



wherein Ar is a paratolyl group and M is potassium

The additive masterbatch and polycarbonate pellets were blended on a rotating blender (Lightnin blender) for one minute with agitation. The resultant blended material was gradually fed to a 30 mm twin screw extruder having a 250 °C barrel temperature. The extruded pellets were post blended on a paint shaker to ensure uniform mixing.

The 15 percent IR concentrate was let down in or blended with a base polycarbonate at a 10 to 1 ratio. The base polycarbonate had a 15 gms/10 minute melt flow rate (MFR). The mixture was blended on Lightnin blender for 1 minute. The blended pellets were extruded on 30 mm twin screw extruder at 275 °C barrel temperature to make a 15 MFR ignition resistant polycarbonate product. The final product was dried in an oven for 3 hours at 125 °C and molded into bars for flammability and Izod impact tests. If desired, the IR concentrate and base polycarbonate can be fed separately into the twin screen extruder or can be directly molded into various parts.

Example 2

The procedure for Example 1 was repeated using 1 gm (1 percent) paratolylsulfimide (HPTSM) in place of the KHSO₄.

Example 3

The procedure for Example 1 was repeated using a 30 weight percent IR concentrate. This concentrate contained

2 percent potassium paratolylsulfimide,
2 percent potassium bisulfate,
6 percent fibril-forming
polytetrafluoroethylene and
20 percent tetrabromobisphenol-A oligomer.

This 30 percent concentrate was blended with a base polycarbonate at a 20 to 1 letdown ratio.

Example 4

The procedure for Example 2 was repeated using the above 30 percent IR concentrate at a 20 to 1 letdown ratio.

Control A

The procedure for Example 1 was repeated using only the base resin without either IR concentrate or IR masterbatch.

Control B

The procedure for Example 1 was repeated using only 1.5 percent IR additive masterbatch without concentrate.

The above examples and controls were tested for Izod impact strength and the results are shown in Table I.

Table I

Sample	PC carrier (MFR in gms/10 min.)	Izod Impact 10 mil (0.254 mm) notched at 25 ° C; ASTM D-259-84	
		Izod Impact ft. lb/in (J/m)	% Brittle
Cntrl A (Base Polymer)	N.A.	15.0(800)	0
Cntrl B (Cntrl A + 1.5% IR Masterbatch)	N.A.	3.0(160)	100
Example 1 15% I.R. concentrate with 10:1 letdown	22	14.5(775)	0
Example 2 15% I.R. concentrate with 10:1 letdown	22	14.7(785)	0
Example 3 30% I.R. concentrate with 20:1 letdown	22	13.0(694)	10
Example 4 30% I.R. concentrate with 20:1 letdown	22	13.3(710)	10

Table 1 shows that the use of IR concentrate at either 10 to 20 to 1 letdown (15 or 30 percent) resulted in improved Izod impact properties without any brittle breaks versus IR additive masterbatch which resulted in very low Izod impact with 100 percent brittle breaks. The improvement of Izod impact via the use of IR concentrate is attributed to more uniform additive dispersion using IR concentrate than using IR masterbatch.

The above examples and controls were further tested for ignition resistance or flammability using the well known UL-94 test. The results are shown in Table II.

Table II

Sample	UL-94 Test, 1/16" (1.6 mm)		
	Avg. T-Sec	Number of Drips	Rating
Control A	10.3	5/5	V-2
Control B	1.0	0/5	V-0
Example 1	1.2	0/5	V-0
Example 2	1.5	0/5	V-0
Example 3	1.1	0/5	V-0
Example 4	1.3	0/5	V-0
Note: T-Sec means time in seconds for a flame out			

Table II shows the use of IR concentrate does not detract from the flammability properties of final product.

Example 5

The procedure for Example 3 was repeated using a 20 MFR polycarbonate carrier.

Example 6

The procedure for Example 4 was repeated using a 15 MFR polycarbonate carrier.

Example 7

The procedure for Example 4 was repeated using a 10 MFR polycarbonate carrier.

Control C

The procedure for Example 3 was repeated using a 40 MFR polycarbonate carrier.

Control D

The procedure for Example 3 was repeated using a 80 MFR polycarbonate carrier.

The above examples and controls were tested for Izod impact strength and the results are shown in Table III.

Table III

Sample	PC Carrier (MFR)	Izod Impact 10 mil (0.254 mm) notched at 25 °C; ASTM D-259-84	
		Izod Impact (ft.lb./in)	% Brittle
Cntrl A (Base Polymer)	N.A.	15.0(800)	0
Cntrl C (Cntrl A + 30% IR concentrate at 20 to 1 ratio)	40	7.5(400)	50
Cntrl D (Cntrl A + 30% IR concentrate at 20 to 1 ratio)	80	3.0(160)	100
Example 5 (Cntrl A + 30% IR concentrate at 20 to 1 ratio)	20	13.0(694)	0
Example 6 (Cntrl A + 30% IR concentrate at 20 to 1 ratio)	15	14.5(775)	0
Example 7 (Cntrl A + 30% IR concentrate at 20 to 1 ratio)	10	14.0(747)	10

The above controls and/or examples show that high melt flow rate polycarbonates are not effective as carriers as the low MFR carriers.

The above examples and controls were further tested for ignition resistance using the UL-94 test. The results are shown in Table IV.

Table IV

Sample	UL-94 Test, 1/16" (1.6 mm)		
	Avg. T-Sec	Number of Drips	Rating
Control A	10.3	5/5	V-2
Control C	1.0	0/5	V-0
Control D	2.0	0/5	V-0
Example 5	1.0	0/5	V-0
Example 6	1.0	0/5	V-0
Control 7	1.0	0/5	V-0
Note: T-Sec means time in seconds for a flame out			

Tables III and IV show that lower MFR polycarbonate carriers help to improve the Izod impact strength of the polymer better than higher MFR PC carriers without sacrificing the flammability property of the final product.

Claims

1. A process for dispersing powdered ignition resistant additives into carbonate polymers to make polymers having an embrittlement of 10 percent or less which comprises
 - 5 A) preparing a base concentrate by blending a carbonate polymer having a melt flow rate in the range of from 3 to 80 with said powdered ignition resistant additives;
 - B) pelletizing said base concentrate;
 - C) blending said concentrate pellets with carbonate polymer pellets having a melt flow rate of from 1 to 80 and substantially lower than said first carbonate polymer whereby the additive composition in said polymer/concentrate blend is present in an amount effective to render said blend ignition resistant; and
 - 10 D) pelletizing or molding said carbonate polymer/concentrate blend.
2. A process as claimed in Claim 1 wherein the additives consist of a mixture of a metal salt of an aromatic sulfur containing compound, a monomeric, oligomeric or polymeric halogenated aromatic compound, a metal salt of an inorganic compound or a free aromatic sulfimide, and a fibril-forming poly-
 15 tetrafluoroethylene.
3. A process as claimed in Claim 2 wherein the additives consist of an alkali metal salt of paratolylsulfimide, tetrabromobisphenol-A oligomer, an alkali metal sulfate salt and fibril-forming polytetrafluoroethylene.
4. A process as claimed in Claim 1 wherein the polycarbonate polymer in step A) and step B) is a bisphenol A polycarbonate and the additives comprise:
 - 20 i) from 2.0 to 10 percent by weight of a metal salt of an aromatic sulfur containing compound,
 - ii) from 10 to 80 percent by weight of a monomeric, oligomeric or polymeric halogenated aromatic compound,
 - iii) from 2.0 to 10.0 percent by weight of compound selected from a metal salt of an inorganic compound and a free aromatic sulfimide, and
 - 25 iv) from 6 to 40 percent by weight of a fibril-forming polytetrafluoroethylene.
5. A process as claimed in Claim 1 wherein in step A) a carbonate polymer having a melt flow rate of from 3 to 20 is dry blended with from 5 to 80 weight percent of said additives.
6. A process as claimed in Claim 5 wherein the polycarbonate polymer in step A) is a polycarbonate resin homopolymer made from bisphenol A and has a melt flow rate of from 3 to 20.
- 30 7. A process as claimed in Claim 4 wherein said aromatic sulfur-containing compound is an aromatic sulfonate, aromatic sulfate, aromatic sulfonamide or aromatic sulfimide.
8. A process as claimed in Claim 4 wherein the aromatic sulfimide additive consists of an alkali metal salt of paratolylsulfimide.
9. A process as claimed in Claim 4 wherein said halogenated aromatic compound is
 35 tetrabromobisphenol-A oligomer.
10. A process as claimed in Claim 4 wherein said metal salt of an inorganic compound is potassium bisulfate and said free aromatic sulfimide is paratolylsulfimide.

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European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 12 3428

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y,D	US-A-4 626 563 (THE DOW CHEMICAL COMPANY) * column 4, line 20 - column 4, line 39; claims 1-8 * - - -	1-10	C 08 J 3/22 C 08 K 13/04 C 08 L 69/00 //
Y	US-A-3 166 606 (UNION CARBIDE CORPORATION) * column 8, line 1 - column 9, line 65; claims 1-6 * - - -	1-10	(C 08 L 69/00 C 08 L C 08 L 27:18)
A	EP-A-0 000 186 (BAYER AG) * claims 1-10 * - - -	1-10	
A	EP-A-0 046 558 (MOBAY CHEMICAL CORPORATION) * page 11, line 5 - page 11, line 28; claims 1-2 * * page 13 * Comparison example (aa) + (2) @ page 14, line 14 - page 14, line 15 * * page 15 * Control example (c) * - - -	1-10	
A	EP-A-0 213 466 (GENERAL ELECTRIC COMPANY) * claims 1-10 * - - - - -	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 J C 08 K C 08 L
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		31 January 91	OUDOT R.
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone		E: earlier patent document, but published on, or after the filing date	
Y: particularly relevant if combined with another document of the same category		D: document cited in the application	
A: technological background		L: document cited for other reasons	
O: non-written disclosure		&: member of the same patent family, corresponding document	